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TENSILE BEHAVIOUR OF ULTRA VIOLET (UV)-IRRADIATED FILMS OF NATURAL RUBBER (NR)/POLY (VINYL ACETATE) (PVAc) BLENDS

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ABSTRACT

The effect of UV radiation doses on the blends of PVAc/NR films was thus studied by measurement of tensile strength properties of films derived from blends containing 0, 25, 40 and 50 Mass % PVAc. The results obtained indicate a sudden rise initially in percent elongation for pure natural rubber (0% PVAc) at 50h irradiation time, after which the elongation gradually decreased with further irradiation. In the case of the blends, there was a sudden drop observed in elongation at 50h irradiation but thereafter, the tensile elongation became more or less stable up to 300hrs. The effect of PVAc in stabilizing the blends at longer hours of UV irradiation was noticed. Comparison between the effect of PVAc and conventional fillers in NR, namely TiO_2 and CB have shown results that proved that PVAc only acts as reinforcing filler in the rubber matrix.

KEYWORDS: UV-irradiation, elongation, blends, tensile behavior, natural rubber, dispersion.

INTRODUCTION

Natural rubber (NR) based products are widely demanded for variety of applications. In the household, aviation and space industries, rubber products are playing significant functions to provide comforts in human life (Jalham and Maita, 2006). Rubber is usually the base material in a product that requires rubber like elasticity and flexibility. However, natural rubber (NR) being essentially poly (cis-1, 4-isoprene) and containing unsaturation is susceptible to autoxidative degradation in presence of ultraviolet (UV) radiation, with the attendant consequences of loss of useful application properties. . Sometimes, rubber products require stiffness along with flexibility, often in specific direction (Geethamma *et al*., 2005). This necessitates modification of NR in order to tailor its properties in line with area of intended application. In particular, it can be suitably modified to improve its vulnerability to UV-induced degradation. One of the strongest points which inform the high demand for NR as an industrial raw material is based on its intrinsic ability of readily yielding to either physical or chemical modifications to give products with a wide range of properties. Polymer blending offers an extraordinary rich range of new materials with enhanced characteristics regarding optical, chemical or mechanical performances (Paul and Barlow, 1980; Ruzette and Leibler, 2005).

On the other hand, poly (vinyl acetate) (PVAc) is a thermoplastic, synthetic polymer with saturated carbon stem and, hence having high resistance to UV radiation. Due to presence of the pendant bulky acetate groups on the chain, which offers resistance to free rotation, PVAc is also a relatively stiff polymer (Pizzi, 1983). In this paper, PVAc was, therefore, blended with natural rubber using latex blending technique, to obtain films. The products are expected to demonstrate improved resistance against the deleterious effects of UV radiation relative to virgin NR, on one hand and, secondly enhanced flexibility compared to virgin PVAc. The effect of UV irradiation was studied by measuring the tensile properties of films of the blends of PVAc and NR before and after exposure to UV radiation doses.

EXPERIMENTAL SECTION

Materials

The PVAc emulsion used in this study was supplied by Makeean Polymers CC., Pretoria, South Africa while the NR latex was purchased from Noma Glory Enterprise, Benin City, Nigeria. The characteristics of the materials are given in Table 1. Both polymers were used as purchased without need for further purification.

Table 1. Materials used for the experiment

Materials	Research code	Source	Remarks
Polyvinyl acetate emulsion	PVAc (M55)	Makeean Polymers CC, Pretoria, South Africa	Solids contents, 51%; viscosity, 12000-20000 (cp); pH, 4-5
Natural rubber latex	NR	Noma Glory, Benin City, Nigeria	Dry rubber contents, 61.5%; viscosity, 300 (cp); pH, 9-10
TiO_2 dispersion	XK Dispersion	ICC Pty, South Africa	Solids contents, 72.8%; pH, 7.0
Carbon black (CB)	XB Dispersion	ICC Pty, South Africa	Solids contents, 59.2%; pH, 7.0

Preparation of Blends

The blends of PVAc emulsion and NR latex were prepared using the latex blending method as described by Ochigbo (Ochigbo *et al*., 2009). It consists of mixing PVAc emulsion directly with ammonia-stabilized natural rubber latex concentrate under low shearing force at ambient temperature until a homogeneous mixture resulted. Blends made of 0, 25, 40, and 50 mass percent PVAc were prepared using this method. Blend films were prepared by casting immediately on non-sticky transparent polyester sheet (Pelikan Overhead TF 100 PE) and using a 500μm (i.e. 0.5 mm) gauge doctor blade to maintain constant film thickness. The sheet with the wet films were then placed under atmospheric conditions (approximately, 27^{o}C) for air-drying until the cast no longer adhere to the hand when touched. Similar samples were made and subjected to UV irradiation for drying using an accelerated weather testing machine (Model: QUV, USA). These samples were exposed to UV radiation doses for 50, 100, 200 and 300 hours, respectively. The final average thickness of dry films ranged from 155-300μm, as measured by hand thickness gauge (Mitutoyo Digimatic Indicator, Japan).

Tensile Testing

Dumb-bell specimens were punched directly from the films on the polyester substrates and were freed from the substrates. The mechanical strength of the free films was determined using tensile tests, which were performed in accordance with ASTM D632-882 test method, on a Lloyd Instruments LRX Plus, TG 34 tensile testing machine at a crosshead speed of 50 mm/min. The results of at least five samples for a given blend from both air-dried and UV-cured processes were obtained and reported as averaged values.

RESULTS AND DISCUSSION

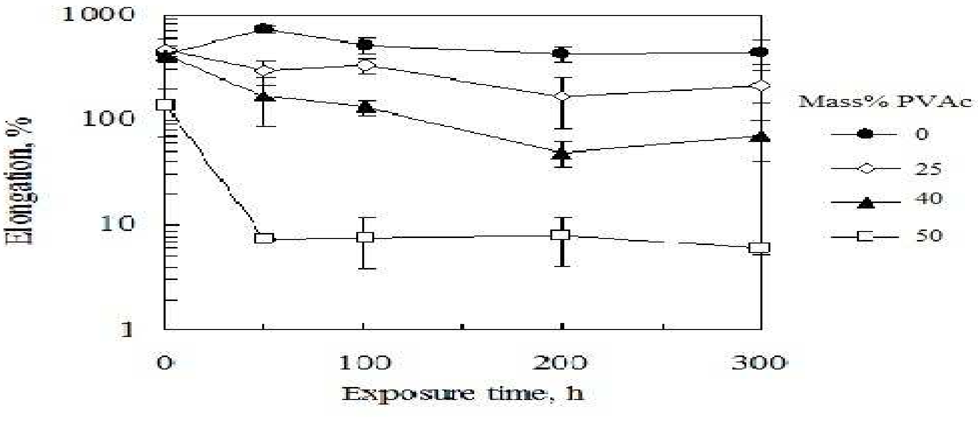

Figure 1. Elongation (%) at break of some blends against UV radiation exposure (h)

The results of tensile elongation properties obtained for samples dried in air (0 h) and those due to different UV irradiation doses are summarized as shown in Figure 1. The tensile elongation of the blends in general tends to increase with decrease in PVAc (or increase in NR) content. Since NR is an elastomer (which refers to a molecule that is capable of undergoing long range reversible elongation), it is expected that the introduction of NR should results in increased elasticity for that substance. Consequently, the blend containing 50% PVAc (highest concentration of PVAc fraction in the blends) presented the lowest elongation-at-break. With the exception of pure NR, it is seen that the tensile elongation is at maximum for each sample at 0 h of UV irradiation (air-dried), but generally dropped afterward on initial exposure (50 h) to UV doses. This obviously suggested that the exposure to UV doses limits tensile behaviour of the blends. Compared to other blend samples, the blend having 50% PVAc decreased the most sharply after 50 h of UV exposure but afterward became more or less constant with continued doses of UV exposure. This significant marked initial drop in tensile elongation for this sample is due to the UV irradiation impact on one hand, and possibly also poor interfacial adhesion between the PVAc and NR components. It is suggested that miscibility and, hence interfacial adhesion, is decreased when PVAc fraction increases relative to NR component in the blends. In other words, the miscibility between the blend components is dependent upon which component is serving as dispersed phase (i.e the component in smaller amount). Usually, for every blend, the component in larger amount acts as a continuous phase (Fox and Allen, 1991). The subsequent constancy in the tensile property of this sample (50% PVAc) with further UV doses might be due to hardening of the plastic content attributable to molecular re-arrangement. As seen this effect is less in the remaining two blends (40% & 25% PVAc) containing lesser amounts of PVAc content.

In the case of pure rubber (0% PVAc), there was first a sudden rise in tensile elongation at 50h irradiation time before a gradual decrease is noticed with UV exposure doses. This initial increase in tensile elongation observed for pure NR was most likely due to onset of cross-linking reactions as similar to vulcanization of rubber which usually results in increased rubber elasticity, and hence tensile elongation. In this case, it is assumed that a mechanism known as oxidative polymerization is responsible for the crosslinking reactions (Scheme 1).

Initiation: Generation of polymer radicals (R^*) from rubber molecule (RH)

$$RH \xrightarrow{\text{UV irradiation}} R^* + (H^*) \qquad \text{(i)}$$

Alternatively, oxygen can bring about the formation of polymer radicals as stated below.

$$RH + O_2 \longrightarrow R^* (+ HO^*_2) \qquad \text{(ii)}$$

Propagation: Formation of peroxyl polymer radical (RO^*_2) followed by polymer hydroperoxide (ROOH)

$$R^* + O_2 \longrightarrow RO^*_2 \qquad \text{(iii)}$$

$$RO^*_2 + RH \longrightarrow ROOH + R^* \qquad \text{(iv)}$$

The resulting hydroperoxides are capable of undergoing decompositions via the pathways listed below.

$$ROOH \longrightarrow RO^* \text{ (alkoxyl radical)} + {}^*OH \qquad \text{(v)}$$

$$ROOH \longrightarrow R^* + {}^*OOH \text{ (hydroperoxy radical)} \qquad \text{(vi)}$$

$$ROOH \longrightarrow RO^*_2 + H \qquad \text{(vii)}$$

Termination: This stage includes all processes leading to formation of various inactive products. The chain reactions thus come to halt.

$$2R^* \longrightarrow R{-}R \text{ (a C-C crosslink)} \qquad \text{(viii)}$$

$$RO^*_2 + R^* \longrightarrow ROOR \text{ (polymer peroxide)} \qquad \text{(ix)}$$

$$RO^*_2 + RO^*_2 \longrightarrow ROOR + O_2 \qquad \text{(x)}$$

Scheme 1: Schematic representation of the possible mechanism of oxidative crosslinking reactions of natural rubber molecule

Reaction (x) occurs when oxygen pressure is high, while (ix) takes place in solid state when sufficient oxygen concentration cannot be maintained in the system.

It is assumed that the formation of the crosslinks is responsible for observed initial increased tensile elongation of the natural rubber at 50h UV dose. On longer exposure to the UV dose, the crosslinked products likely undergo intramolecular cleavages (‘ageing’) accompanied by loss of mechanical properties, including tensile elongation. Whereas the formation of initial crosslinks in natural rubber might lead to enhanced elastomeric property, the same phenomenon leads to chain hardening in saturated polymer molecule, such as poly (vinyl acetate) present in these blends as second component.

Thus, oxidative polymerization, also termed “drying” arises because of reaction of oxygen with the hydrogen atoms alpha to the double bonds present in the natural rubber molecule. The process leads to crosslinking reactions resulting eventually to thin solid film. As expected the subsequent decrease with further UV exposure might be due to ageing (chain scission). Overall, the results followed similar pattern as has been previously reported by Khan *et al* (2006) with polymer films of sago starch/polyvinyl alcohol cured by UV radiation.

In view of the poor compatibility between NR and PVAc, especially with increase in the latter in the blends, it is assumed that PVAc only acts as reinforcing filler to the rubber matrix. In order to check the reliability of this assumption, samples were prepared in which the natural rubber was filled with aqueous dispersions of titanium dioxide, TiO_2 and carbon black, respectively in amounts equal to the same volume filler as PVAc blend. The result of this is shown in Figure 2.

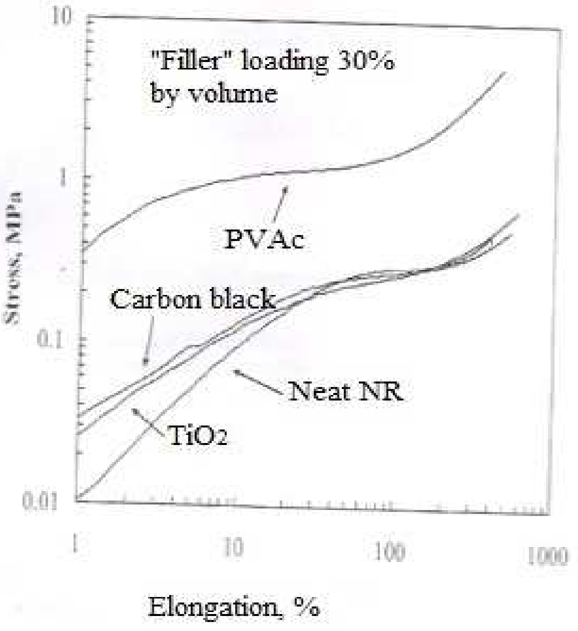

Figure 2. Comparison between the reinforcing effects of PVAc-filled rubber with TiO_2 or CB-filled rubber at fixed volume fraction of 30%

From the results obtained, it was observed that the two pigment-filled natural rubber samples showed similar stress-extension behaviours. The stress curves were many folds higher than that of neat rubber at low extensions. However, at higher extensions they approached asymptotically the pattern shown by pure rubber. This contrasted with the performance of natural rubber containing the same volume fraction of PVAc whose stress-strain curve was observed to lay some order of magnitude higher.

CONCLUSION

The influence of UV irradiation doses on the PVAc blends containing different amounts of NR has successfully been investigated. Whereas pure NR showed an initial increase in tensile elongation, attributable to crosslinking reactions, as similar to vulcanization process, all the blends showed decrease in the same property with initial UV exposure. Comparison between the effect of PVAc and conventional fillers in NR, namely TiO_2 and CB have shown results that proved that PVAc only acts as reinforcing filler in the rubber matrix.

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